

# CONTRIBUTION OF MINERAL MATTER TO LOW TEMPERATURE LIQUEFACTION MECHANISMS.

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## Introduction

The pathways by which coal macromolecules can be depolymerised to give lighter products have long been sought by coal scientists and the precise roles of individual functional groups in the reactions which occur during liquefaction are still not clear. Generally, radical reactions for hydrogen incorporation are dominant at temperatures  $\geq 350^\circ\text{C}$ . However, reactions of coals are not necessarily limited to free radical processes. Recently, the existence of non-radical pathways has been proposed, upon the observation of a higher gas-phase  $\text{H}_2$  consumption observed in comparative non-catalytic runs with raw and dried low rank coals at  $350^\circ\text{C}$  [1]. However, the preliminary data largely ruled out the possibility that, under the conditions employed, there was non-radical incorporation of molecular  $\text{H}_2$  into coal. It was therefore proposed that the reaction of  $\text{H}_2$  may be mineral matter catalysed.

To date, the exact role of much of the mineral matter in coals remains unclear [2-4]. These mineral and inorganic species can act as catalysts or poisons during liquefaction depending on reaction conditions. The physical role of minerals could be to block access to pores or reaction sites. Conversely, the chemical roles of inorganics include: clays which can act as cracking catalysts and the hydrogenation catalyst, pyrite. Catalytic activity, mainly attributed to pyrite, is well documented [2, 5]. Conversely, removal of naturally occurring anions such as  $\text{Na}^+$ ,  $\text{Ca}^{2+}$  and  $\text{K}^+$  has been shown to enhance liquefaction conversions [4,6] and several authors have observed a favorable influence of demineralization on coal depolymerization. Shams et al. [7] reported that the treatment of coals with methanol and HCL removes virtually all of the calcium species, leading to retardation of the retrogressive reactions Ca was proposed to catalyse.

The aim of the work reported here was to evaluate the nature and distribution of coal mineral matter in both untreated and treated (demineralized) samples of Wyodak coal, and consider the influence of these compounds by assessing their possible catalytic effect. To date, a series of experiments has been undertaken to compare the effect of demineralization on coal conversion at low temperatures (ca  $300\text{--}350^\circ\text{C}$ ), where preliminary results indicated that conversions were comparable upon pretreatment.

## Experimental

**Demineralization** Wyodak coal (DECS-8),  $\leq 60$  mesh, was obtained from the Penn State Coal Sample Bank; proximate and ultimate analyses are listed in Table 1[8]. Demineralisation was facilitated by successive acid treatments. The first stage was an HCl wash (10 ml per gram of coal) to remove any alkaline earths which would form insoluble fluorides at the HF wash stage. This was stirred at  $60^\circ\text{C}$  for 1 hour, filtered and washed. In the second stage, a 40% HF solution (10 ml per gram of coal) was digested at  $60^\circ\text{C}$  for 1 hour. The final sample was thoroughly washed with distilled water to ensure removal of residual HF. The filtrate was tested with  $\text{AgNO}_3$  to indicate the presence of any residual chloride ions.

**ICP-AAS** Both the untreated and demineralised samples were analysed by ICP-AAS to more clearly identify the mineralogical distribution changes upon acid treatments. Samples were ashed at  $950^\circ\text{C}$  and the ash dissolved using a lithium metaborate fusion technique. Solutions were then analysed using a Leeman Labs PS3000UV inductively coupled plasma spectrophotometer (ICP).

**Liquefaction** The demineralised coal samples were dried in a vacuum oven at  $110^\circ\text{C}$  for 2 hours prior to use. Liquefaction was carried out in a 25 ml tubing bomb with ca 4g coal, at 300 and  $350^\circ\text{C}$ , 1000 psi  $\text{H}_2$  or  $\text{N}_2$  for 30 min. When solvent was present, the coal:solvent ratio was 1:1 w/w; both H-donor (tetralin) and non-donor solvents (1-methyl naphthalene) were utilised. The gaseous products were collected and analyzed by GC; the liquid and solid products were recovered and separated by sequential Soxhlet extraction into *n*-hexane solubles (oils), toluene solubles (asphaltenes) and THF solubles (preasphaltenes). The THF-insoluble residue was washed with acetone followed by *n*-pentane to remove any residual THF. All recovered products were finally dried under vacuum at  $110^\circ\text{C}$  for ca 10 hours. The conversion of coal into soluble products and gases was calculated on the basis of recovered THF-insoluble residue and reported on a dmmf basis. Residues were further analysed by FTIR and  $^{13}\text{C}$  NMR.

**FTIR** Fourier transform infrared (FTIR) spectra of the demineralised coal and liquefaction residues were recorded on a Digilab FTS-60 spectrometer by co-adding 400 scans at a resolution of  $2\text{ cm}^{-1}$ . The samples were prepared as KBr discs; predried sample (3 mg) was mixed with KBr (300 mg). All spectra were baseline corrected.

**$^{13}\text{C}$  NMR** Solid state  $^{13}\text{C}$  NMR spectra were recorded on a Chemagnetics M-100 NMR spectrometer using the cross polarization magic angle spinning (CP-MAS) technique. The measurements were carried out at a carbon frequency of 25.1 MHz.

## Results and Discussion

### ICP-AAS

As summarised in Table 2, metal concentration was determined by ICP-AAS in the normal and demineralised Wyodak coal samples. Ash was determined as 8.94 wt%. Upon demineralisation, ash concentration fell to ca 0.37 wt%, with the corresponding metal concentrations as indicated. All values are expressed in weight percent on an ash basis with the exception of HTA, which is on an as-received basis.

### Liquefaction Data

Results for the reactions conducted at 350 °C, both in the presence and absence of solvent, are reported in Table 3. For purposes of initial comparison, these will be discussed with respect to data with untreated Wyodak coal [1]. It is clearly demonstrated that demineralization imparts no seriously detrimental effects on liquefaction under such conditions.

The overall conversions and liquid product distribution indicates that the most significant changes occur in the presence of solvent, both H-donor and non-donor. In the absence of solvent, conversion can be considered to be solely due to pyrolysis, i.e. there are no solvent dissolution or H donation contributions. Higher conversion is the result of increased gas yield rather than liquid yield and quality. This may be derived from two contributions. If the reduction in Fe concentration, as highlighted by ICP, also comprises pyrite, this would account for the decrease in liquid yield. Moreover, if the increased gas make is due to  $\text{CO}_2$  removal of the mineral matter may be considered to promote more facile pyrolysis of  $-\text{COOH}$  versus  $-\text{COO}^-\text{M}^+$ .

Reaction in the presence of the non-donor solvent, 1-methyl naphthalene, results in increases in both gas and liquid yield relative to the no-solvent situation. With "normal" coal and 1-MN, the increase in liquid yield for the raw coal is 5.1%. Presumably this increase is the "extra" liquid dissolved out by the solvent. With demineralised coal and 1-MN, the increased liquid yield is 12.4%. Therefore, the solvent is undoubtedly better able to dissolve material from the demineralised coal. This suggests that there is improved access of the solvent to the coal interior upon removal of mineral species.

The best liquid conversion, defined by oil concentration as a fraction of the total liquid yield, occurs upon reaction with tetralin. This is not surprising because tetralin is an H donor, thus any enhancement in tetralin conversion relative to 1-MN can be attributed to H donation. The increase in liquid yield for normal coal in tetralin, relative to 1-MN, is 7.4%; the increase for demineralised coal is 8.6%. The difference in these numbers is within experimental error,  $\pm 3\%$ , hence demineralisation has no effect on H transfer from tetralin and there is no mineral matter catalysis of H donation.

Table 4 summarises the results of liquefaction conducted under an inert  $\text{N}_2$  atmosphere and those facilitated in  $\text{H}_2$ . No significant deviation in overall conversion or product distribution was observed, even in the presence of solvent.

There are similarities between the results presented here and those of other studies, not necessarily limited to demineralised samples. Tomic and Schobert [9] also observed solvent effects under mild liquefaction conditions of subbituminous coals; the addition of a solvent was observed to enhance conversion relative to the reaction with no solvent, similar to the results in Table 3. And if, indeed, pyrite concentration has been reduced, the results in Table 4 confirm those reported by Tomic and Schobert [9], Artok [10] and Huang [11] who similarly reported that utilization of  $\text{H}_2(\text{g})$  is ineffective without a good hydrogenation catalyst, as illustrated by the similarities in the comparative  $\text{H}_2$  and  $\text{N}_2$  runs. Serio et al. [4], also reported enhanced conversion for low rank coals following demineralization. This raises questions as to possible contribution of mineral species to low temperature liquefaction mechanisms. Joseph [6] ascribed this phenomenon to cations inhibiting hydrogen transfer from donor solvent/gaseous hydrogen to free radicals, in effect promoting retrogressive reactions. Therefore, it could be that the absence of these species allows for better access to reactive sites in the coal interior.

**FTIR** Comparative FTIR spectra of the normal and demineralised coal and associated residues are shown in Figures 1 and 2. The spectrum of the whole demineralised coal indicates the presence of most of the groups of interest in this study.

Hydroxyl groups at	3300-3600 $\text{cm}^{-1}$
Aromatics	3030 $\text{cm}^{-1}$ and associated bands at 1450-1600 $\text{cm}^{-1}$
Aliphatics	2920, 2850 $\text{cm}^{-1}$
Carboxylic acids	1710-1760 $\text{cm}^{-1}$
Conjugated Ketones	1715 $\text{cm}^{-1}$
Esters	1712-1735 $\text{cm}^{-1}$ (present as a shoulder on the C=O band)

After reaction under H<sub>2</sub> at 350 °C, the most notable feature of the whole product spectrum is a decrease in hydroxyl concentration, in part attributed to a loss of H<sub>2</sub>O. Further examination of the THF-insoluble residue from this experiment confirms the loss of OH functionality coupled with the disappearance of the ester shoulder. The FTIR spectrum of the THF-insoluble residue from the reaction conducted with tetralin displays somewhat contrasting features. The carboxyl stretching region is much broader; moreover, the ester shoulder is more pronounced and the carbonyl region is much more defined.

The FTIR spectra of the THF-extracted raw coal and the residues from the runs conducted at 350 °C under N<sub>2</sub> demonstrated that under all conditions, i.e. both in the presence and absence of solvent, no marked changes were observed. The residue from these sets of experiments is currently undergoing further analysis by Py-GC-MS, to evaluate in more detail the fundamental differences in speciation resulting from non-catalytic treatment under different regimes.

**Solid State <sup>13</sup>C NMR** The <sup>13</sup>C CP-MAS spectra of the normal and demineralised coal is shown in Figure 3. The <sup>13</sup>C CP-MAS spectrum of the demineralised Wyodak displays many similarities to that of the untreated coal. The region between 0 and 80 ppm consists primarily of aliphatic carbons, e.g. methoxy groups and the symmetry of this band should be noted. The second region of interest between 90 and 170 ppm is due to the presence of aromatic carbon. The shoulders present on the side of the aromatic band may be attributed to specific functionalities, e.g. catechol groups (at 142 ppm) and phenolic groups (at 152 ppm). The carboxylic functionality is prominent at 180 ppm, similarly for the carbonyl at ca 210 ppm. In the aliphatic band, the symmetry observed for the parent coal is lost, and the appearance of a shoulder at ~25 ppm is observed. This may be attributed to a number of groups, including CH<sub>3</sub>-Ar side chains (20-21 ppm). Furthermore, the distinct shoulders observed in the aromatic region have virtually disappeared, indicating a loss of oxygen functionalities.

### Conclusions

As anticipated, relative to runs at 350 °C with untreated coal, demineralisation affords higher overall conversions; this trend becomes more apparent when either an H-donor (tetralin) or non-donor (1-mn) solvent are used. Specifically, there is no evident mineral matter effect on solvent H donation. Thus, initial results between the two sets of data suggests that the reactions undergone at 350 °C are not mineral matter catalyzed.

With respect to mineral matter identification, further ICP-AAS studies have been conducted, in association with CC-SEM and XRD determinations to identify the mineral phases and species contributing to possible low temperature hydrogenation mechanisms.

### References

1. C. Song, A.K. Saini, H.H. Schobert *Energy and Fuels* **8**, 301 (1994)
2. Maldonado-Hodar, F.J., Rivera-Utrilla, J., Mastral-Lamarca, A.M., Ferro-Garcia, M.A. *Fuel* **74**(6), 818 (1995) and references therein.
3. Mochida, I., Yufu, A., Sakanishi, K., Korai, Y. *Fuel* **67**, 114 (1988)
4. Serio, M.A., Solomon, P.R., Kroo, E., Bassilakis, R., Malhotra, R., McMillen, D. *Am. Chem. Soc., Div. Fuel Chem., Prep.* **35**(1), 61 (1990)
5. Garcia, A.B., Schobert, H.H. *Fuel* **68**, 1613 (1989) and references therein.
6. Joseph, J.T., Forrai, T.R. *Fuel* **71**, 75 (1992)
7. Shams, K., Miller, R.L., Baldwin, R.M. *Fuel* **71**, 1015 (1992)
8. Penn State Coal Sample Bank and Database
9. Tomic, J., Schobert, H.H. *Energy and Fuels* **10** 1996 (in press)
10. Artok, L., Schobert, H.H., Erbatur, O. *Fuel Proc. Tech.* **37**, 221 (1994)
11. Huang, L. PhD. Dissertation Thesis, The Pennsylvania State University, 1995

Table 1. Analysis of Wyodak Subbituminous Coal (DECS-8).

Vol. Matter	Proximate Analysis (as received)			Ultimate Analysis (wt%, dmmf basis)				
	Fixed Carbon	Ash	Moisture	C	H	N	S	O
32.4	29.3	9.9	28.4	75.8	5.2	1.0	0.5	17.5

Table 2. Spectrochemical Analysis of Normal and Demineralised Wyodak Coal Samples by ICP-AAS.

Sample	Ash	Metal Concentration (wt%)				
		Fe	Ca	Mg	Na	K
Normal	8.94	5.53	13.2	3.02	1.12	0.78
Demineralised	0.37	56.8	9.23	1.51	0.20	0.24

Table 3. Results of Non-Catalytic Liquefaction of Normal and Demineralised Wyodak Coal at 350 °C for 30 min. Under 6.9 MPa H<sub>2</sub>.

Pretreatment	Solvent	Product Distribution (% dmmf basis)				
		Gas	Oil	Asph	Preasph	% Conv.
-	-	3.3	2.1	2.6	4.5	12.5
demineralised	-	10.0	0.8	0.4	5.3	16.6
-	Tetralin	4.2	4.1	7.6	10.0	25.9
demineralised	"	12.0	7.1	6.3	14.4	40.3
-	1-MN	4.0	1.1	5.8	7.4	18.3
demineralised	"	7.7	5.6	3.3	10.3	26.9

Table 4. Results of Non-Catalytic Liquefaction of Demineralised Wyodak Coal at 350 °C for 30 min. Under 6.9 MPa H<sub>2</sub> and N<sub>2</sub>.

Gas	Solvent	Product Distribution (% dmmf basis)				
		Gas	Oil	Asph	Preasph	% Conv.
H <sub>2</sub>	-	10.0	0.8	0.4	5.3	16.6
N <sub>2</sub>	-	10.7	1.2	0.7	5.2	17.8
H <sub>2</sub>	Tetralin	12.0	7.1	6.3	14.4	40.3
N <sub>2</sub>	"	10.4	10.3	3.6	17.8	42.1
H <sub>2</sub>	1-MN	7.7	5.6	3.3	10.3	26.9
N <sub>2</sub>	"	8.7	5.8	1.4	8.4	24.4

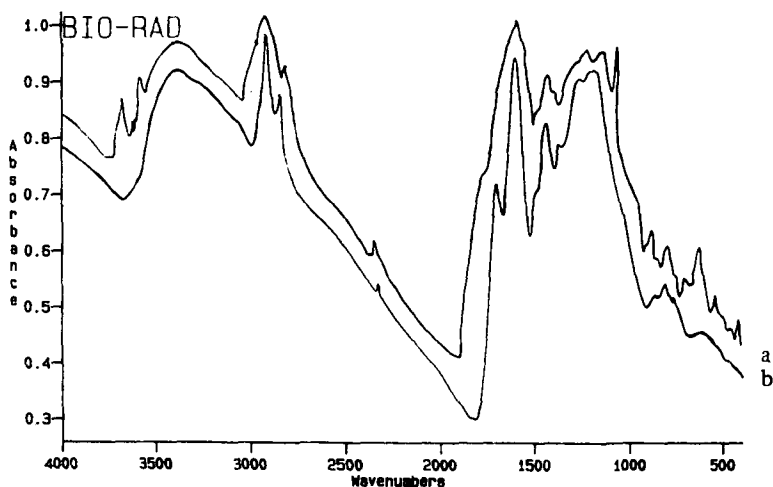


Figure 1. FTIR Spectra of (a) normal and (b) demineralised Wyodak Coal.

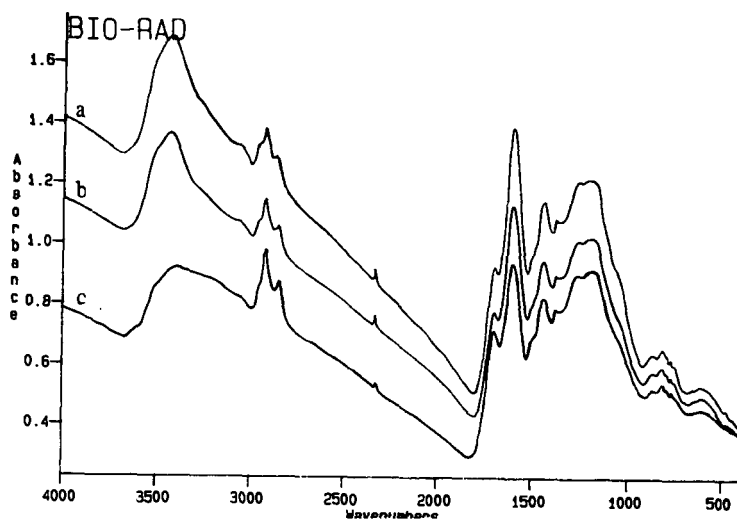


Figure 2. FTIR Spectra of THF-Insoluble Residue from Reaction of Demineralised Wyodak Coal in (a) Absence of Solvent, (b) Presence of Tetralin and (c) Presence of 1-MN.

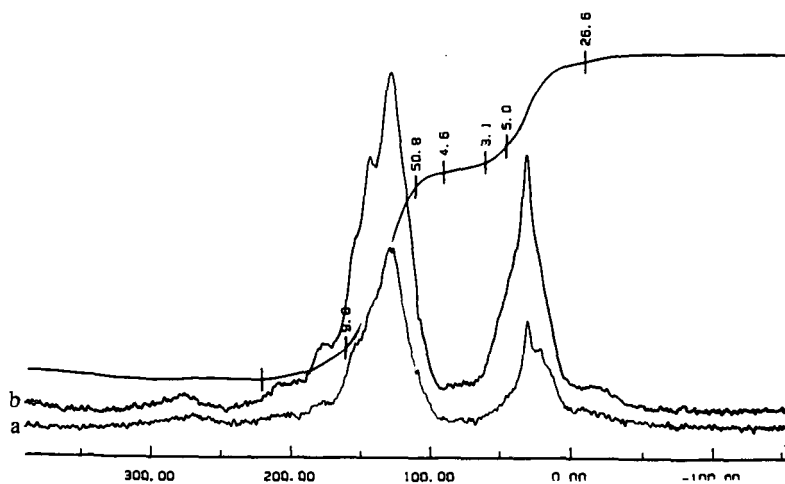


Figure 3.  $^{13}\text{C}$  CP-MAS Spectra of (a) Normal and (b) Demineralised Wyodak Coal.